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# Synthesis of Yttria-Doped $Bi_2o_3$ Nanopowders Via Sol Gel Used in Electrolyte of Solid Oxide Fuel Cell

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***Abstract : Oxide ion conductors have been studied for many years because of their application in devices with high economical interest such as solid oxide fuel cells, oxygen sensors , dense ceramic membranes for oxygen separation. In this paper nanopowders were synthesized via sol gel method. The sintering temperature to complete phase transition are above 500˚c. As-prepared yttria doped Bi2O3 nanocrystals were characterized by X-ray diffraction (XRD) and transmission electron microscope (TEM). Transmission electron microscope (TEM) investigations revealed that the average particle size is less than 30 nm for these powders. It's worth noting that results show a good agreement of both methods. The morphology of the powders were observed on Field Emission scanning electron microscope (FESEM). Ionic conductivity measured by AC impedance spectroscopy.***

**Keywords***:* Nanopowders , Sol-gel , Electron microscopy, Impedance spectroscopy, Substituted
Bi2O3.

**Introduction:** In recent three decades, sol-gel process is developed into a wide research subject. This process due to its reaction in liquid phase, room temperature and the type of the precursors which are applied for obtaining new materials is scientifically and technologically attracts attentions significantly. Over the last decades, Bi2O3-based materials with high oxygen ionic conductivity have been extensively studied for their potential use as solid electrolyte in fuel cell [1]. The delta face-centered cubic (fcc) phase of pure Bi2O3 has high oxide ion conduction at high temperatures, but it is only stable between 730 ºC and 825 ºC (melting point). During cooling from high temperature, large volume change is accompanied with phase transformation from the delta phase into monoclinic alpha phase having low electrical conductivity. Introduction of a proper amount of Yttria (25mol% Y2O3) or some rare earth oxides into the FCC phase stabilizes this structure down to lower temperatures[2-3].

Application of nanocrystalline ceramics can lead to the development of electrochemical devices that have considerably lower operating temperatures and can exhibit significantly improved ionic conductivity [4].

Hence, the present work has been focused on preparation of mixed nanopowders of 75 mol% Bi2O3+25 mol% Y2O3 by sol gel method and fabrication of dense single phase nanocrystalline Bi2O3-Y2O3 solid electrolyte and study of the electrical conductivity.

## 2. Experimental

### *2.1. Raw materials*

Bi (NO3)3.5H2O (98% in purity), HNO3 (67.5% in purity), Y(NO3)3.6H2O, Citric acid (AR grade), PEG4000 ,were purchased from Merck and used as received.

### *2.2. Devices*

XRD diffraction studies were carried out by Philips (PW3710) diffractometer with CuKα radiation source (λ=0.151478 nm).The TEM picture was recorded with Zeiss EM 10C instrument at the accelerating voltage of 100 kV. IR transmittance and absorption spectra were measured on the two samples prepared by KBr pellet technique in the wave number range of 400–4000 $cm^{-1}$ on (FTLA 2000-100) model.

Field emission scanning electron microscopy measurements studies were performed using Hitachi S4160 model. Ionic conductivity was measured by an AC impedance analyzer technique with Model4274A multi-frequency Hewlett-Packard LCR meter in the frequency range of 100 Hz–100 kHz. The sintered pellet was placed between both faces of silver electrodes.

The experiments were carried out in steps of 20 °C from 300°C up to 800 °C with 15 min stabilization time per step.

### *2.3. Synthesis*

Mixed nanopowders of 75 mol% Bi2O3+25 mol% Y2O3 have been prepared by sol gel method. The analytically pure Bi(NO3)3.5H2O and Y(NO3)3.6H2O, in molar ratio of 3: 1, were dissolved in dilute nitric acid to prepare a nitrate solution containing a total metal ion ($B^{3+}$,$Y^{3+}$) concentration of 0.1 mol/L. In order to prevent agglomeration, 3 wt. % PEG4000 (polyethylene glycol of average molecular weight equal to 4000) was added as a surfactant. The solution was continuously stirred using a magnetic needle for 2 h and then a sol formed. The sol was heated to 90 °C for 1h to form a yellowish gel. This gel was decomposed at 160°C in oven .The gel initially started to swell and filled the beaker producing a foamy precursor. This foam consists of homogeneous flakes of very small particle size.The mixed oxide nanopowders synthesized as above were pressed uniaxially into disk-shaped pellets having an outer diameter of 10 mm and a thickness of 1 mm at a relatively low pressure of

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01 April 2014

100 MPa. The samples were sintered at temperatures of 650°C for 2h in order to study the electrical conductivity.

**3-Results and Discussion**

XRD were employed to characterize these powders. The sample was scanned in the 2θ range of 4˚-60˚ for a period of 5 s in the step scan mode. The diffraction pattern (Fig.1) presents peaks corresponding to reflection planes of the cubic structure of metallic bismuth. A small fraction of unidentified phase(s) was observed.

The average crystallite size which has been determined by Debye-Scherer formula:

$$L = \frac{K\lambda}{\beta \cos\theta} \qquad (1)$$

Where L is coherence length, related to spherical particle diameter D=4/3L, λ is the wavelength of X ray (nm), k is a constant (= 0.9 assuming that the particles are spherical), β is the full width in radius at half-maximum (FWHM) of the Highest peak (rad) and $\theta$ is the Bragg angle of the highest peak. The particle size obtained from XRD data is 18.14 nm. The calculated lattice parameter by least square fit are a=5. 496 Å.

When the $Y^{3+}$ cation having smaller ionic radius (r =0.9 Å ) are substituted for $Bi^{3+}$ with larger ionic radius (r =0.96 Å ), the unit cell dimension is likely to decrease. After 2h of sintering time, almost all the α- Bi2O3 had completely transformed into δ-Bi2O3 except for the small traces of free Y2O3 that could still be identified on the XRD pattern. .1h in different magnification In Fig.2. Powders seem to be a continuous and homogeneous material without voids. These powders have a pseudospherical morphology.

| | |
|---|---|
| The elemental analysis of | Dispersive X-ray Analysis |
| (EDAX) using model JEOL | pattern of sample sintered at 650 |
| ºC. | |
| EDAX pattern confirms the | elements in the sample. |

The fine powders were dispersed in acetone and were put on a carbon coated TEM copper grid. The TEM image of the superfine Bi2O3-Y2O3 powder (Fig. 4) shows that nanoparticles are spherical-like shape and the average particle size are less than 20 nm, which was in good agreement with the XRD result.

**Electrical Characterization:**

Impedance spectra for Bi2O3-Y2O3 nanopowders were recorded at temperatures 300, 500 and 600 ºC. The impedance data from the experiment at a given temperatures is presented in the form of Nyquist plots. Nyquist plot at above mentioned temperatures for nanopowders are shown in Fig. 5. The observed complex impedance plots can be modeled using equivalent circuit that contains a circuit shown inset of Fig. 6.

Partially resolved semicircular arcs are observed between1MHz and 100 Hz. The high frequency region semicircular arcs are due to parallel combination of bulk resistance (*R*g) and bulk capacitance (*C*g), which represents grain response of Bi2O3-Y2O3 material [5]. The low-frequency arc may be due to electrode response [6]. The electrical conductivity (logσ) vs. the reciprocal temperature (1000/T) is shown in Fig. 7.

After least squares fitting to the impedance data to obtain the resistances associated with the high and intermediate frequency arcs, the conductivities of the bulk and grain-boundary regions were deduced by accounting for the sample geometry according to Eq. (2):

σ=L /RA (2) Where L is the sample thickness and A is its cross-sectional area.

| | |
|---|---|
| The temperature dependence of conductivity can be represented by Arrhenius equation: | |
| $\sigma = \sigma 0 \exp(-Ea/KT)$ | (3) |

Where $\sigma 0$ is a pre-exponential constant, *E*a is the activation energy for ion migration (eV), *k* the Boltzmann constant and *T* the temperature (K). Based on the above relation, the graph of log $\sigma$ versus 1000/*T* should give a straight line of slope *E*a/*k*, from which activation energy can be calculated.

The ionic conductivity was computed by using the value of real part of the impedance (*Z*') at which imaginary part (*Z*") is minimum. It is observed that ionic conductivity increases with increase in temperature. The ionic conduction is caused by hopping of oxygen ions from lattice site to lattice site under the influence of electric field.

The decrease in diameter of the semicircle fitted for the plot shows decrease in bulk resistance with temperature. The ionic conductivity was found to be increasing with increase in temperature. The change in conductivity at 500° C. (Fig. 7) is similar to the one reported at about the same temperature for Bi2O3 doped with several lanthanides, particularly at low dopant concentrations [7,8,9,10].Based on diffuse scattering results Verkerk et al. have ascribed the change in conductivity to an order– disorder structural transition [7].

However, the plot of the grain interior conductivity vs. reciprocal temperature shows the two regimes usually observed for the bismuth based oxides in which an order–disorder transition is involved. This transition seems to affect ordering of the $O^{2-}$ ions, which are the charge carriers.

**Conclusion:**

In summary, homogeneous nanopowders have been prepared by sol gel method. The single δ-phase is obtained at a temperature lower than that prepared by conventional solid state method. The average size of these nanoparticles ranges less than 20 nm and has an equiaxed morphology which is excellent for better mechanical properties such as high fracture toughness and high ionic conductivity. In sintering process of the mixed nanopowders, the solid solution reaction between Y2O3 and α -Bi2O3 occurred first resulting in the transformation of α -Bi2O3 (monoclinic) into δ-Bi2O3 (cubic) which was stabilized by Y2O3. At lower sintering

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01 April 2014

temperatures, Bi2O3 phase is found to act as a wetting agent of the grain boundaries. The majority of Bi2O3 was segregated at the grain boundaries, because of this behavior; we didn't observe the arc which related to grain boundaries response.

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Table 1. Electrical conductivity and Activation Energy at different temperatures of

| Temperature (◦C) | Electrical conductivity ( $ohm^{-1}$ /cm) | Activation Energy (ev) |
|---|---|---|
| 300 °C | $8.2\times10^{-2}$ | 0.74 |
| 500C° | $1.12\times10^{-3}$ | 0.69 |
| 600C° | $4.3\times10^{-4}$ | 0.51 |

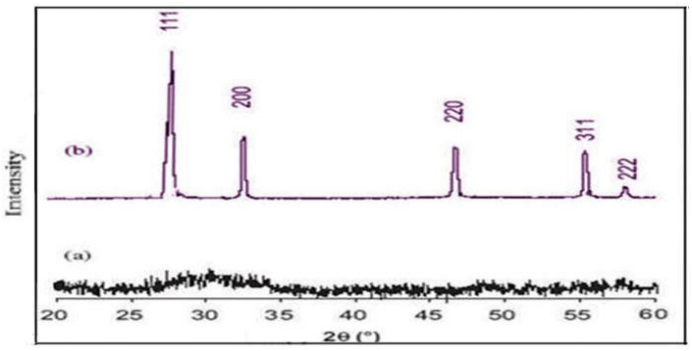


**Fig 1.** XRD pattern of of 75 mol% Bi2O3+25 mol% Y2O3 powder after calcining at 500 °C for 1h.

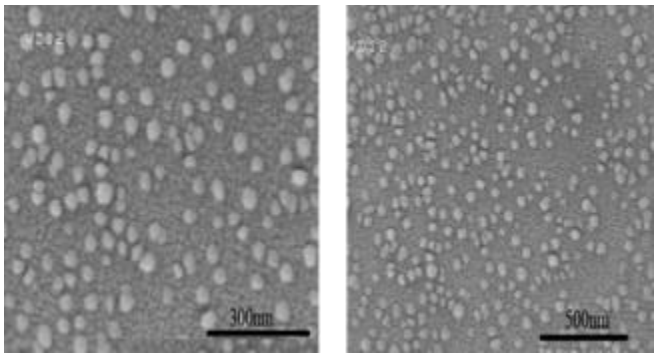


**Fig. 2.** SEM micrographs of Bi2O3-Y2O3 nanocrystalline solid electrolyte calcined at 500 °C for

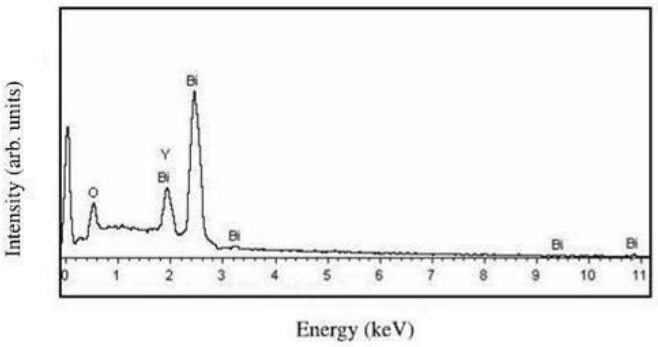


**Fig. 3**. EDAX pattern of Bi2O3-Y2O3 nanocrystalline solid electrolyte calcined at 500 °C for 1h.

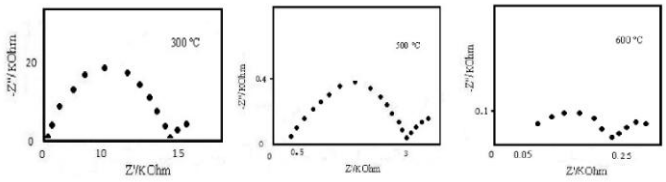


**Fig. 4.** TEM images of the nanoparticles calcined at 650 °C

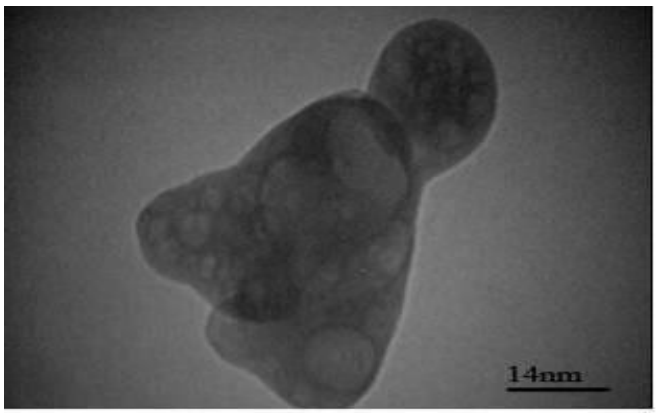


Fig. 5. Impedance (imaginary vs. real part) plots recorded at different temperatures on a sintered pellet of the cubic title

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compound.

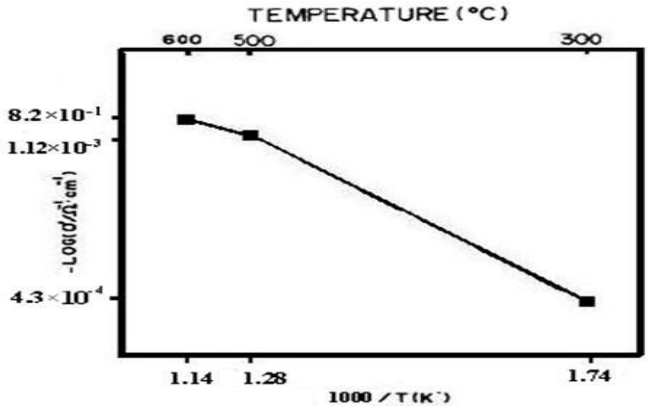


Fig. 6. equivalent circuit of sample.

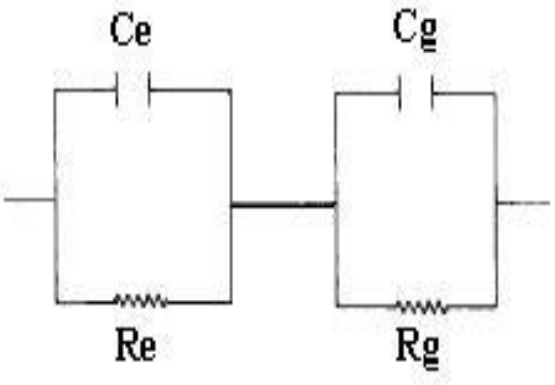


Fig. 7. Arrhenius plot for Bi2O3-Y2O3 nanocrystalline sintered at 650° C.